

PATENT SPECIFICATION

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1373 220

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 (31) Convention Application No. 97311 (32) Filed 11 Dec. 1970
 (31) Convention Application No. 97392 (32) Filed 11 Dec. 1970
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(54) POLYESTER RESINS AND THEIR USE IN
ELECTROSTATIC TONER COMPOSITIONS

ERRATUM

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easy moldability or fuseability, have long been sought. One of the major uses for this type of polyester resin is in the electrophotographic printing art since their relatively low melting point would make them useful in the preparation of electrophotographic inks. The toughness of this type of resin makes the resin easy to handle and facilitates the maintenance of a uniform particle size resulting in clear electrophotographic reproductions.

In xerography, an indirect electrostatic photographic process, it is usual to reproduce a master by electrical photography methods such as, most typically, placing an electrostatic charge on a photoconductive surface, selectively dissipating such charge by exposure to an optical image corresponding to the master to be reproduced, and developing the resulting electrostatic image by decorating with an electroscopic material.

According to one practice in xerography as disclosed in U.S. 2,618,552, the development of the electrostatic image is accomplished by rolling or cascading across the image-bearing surface a developer composition of relatively large carrier particles having on their surfaces, for example electrostatically coated thereon, fine powder particles known as toner particles. As the composition cascades or rolls across the image-bearing surface, these toner particles are electrostatically deposited on and secured to the charged portions of the image and are not secured on the uncharged or

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 14P1E1 14P1X 14P4C 14P5 14P6X D3A
 G2H 5D1A 5D1X 5D1Y 5DY 5G2X 5G3 5GY 5Y

(54) POLYESTER RESINS AND THEIR USE IN ELECTROSTATIC TONER COMPOSITIONS

(71) We, ICI AMERICA INC., (formerly known as ICI North America Inc.) a corporation organised and existing under the Laws of the State of Delaware, United States of America, of Wilmington, Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new polyester resins and their use as binders for toners useful in the art of direct and indirect electrostatic photography. More particularly, this invention relates to non-linear polyesters formed by the condensation of dibasic acids and an etherified diphenol in the presence of an alkoxyated polyhydroxy compound. In addition, this invention relates to electrostatic toner compositions containing the novel polyester resin. The polyester-bound toners are extremely tough and resistable to abrasion and have a relatively narrow melting range.

Polyesters heretofore known usually fall into one of two categories: linear polyesters which are characterized by brittleness and lack of toughness during abrasive handling but which are easily dissolved in unsaturated monomers; or non-linear polyesters which are characterized by inherent toughness and abrasion resistance but which are in general fairly insoluble in unsaturated monomeric solutions and have a relatively high melting point compared to the linear polyester resins. A group of resins which have an inherent toughness and resistance to abrasion, which are relatively soluble in unsaturated monomeric solutions, and which have melting points of less than about 110°C. for easy moldability or fuseability, have long been sought. One of the major uses for this type of polyester resin is in the electrophotographic printing art since their relatively low melting point would make them useful in the preparation of electrophotographic inks. The toughness of this type of resin makes the resin easy to handle and facilitates the maintenance of a uniform particle size resulting in clear electrophotographic reproductions.

In xerography, an indirect electrostatic photographic process, it is usual to reproduce a master by electrical photography methods such as, most typically, placing an electrostatic charge on a photoconductive surface, selectively dissipating such charge by exposure to an optical image corresponding to the master to be reproduced, and developing the resulting electrostatic image by decorating with an electroscopic material.

According to one practice in xerography as disclosed in U.S. 2,618,552, the development of the electrostatic image is accomplished by rolling or cascading across the image-bearing surface a developer composition of relatively large carrier particles having on their surfaces, for example electrostatically coated thereon, fine powder particles known as toner particles. As the composition cascades or rolls across the image-bearing surface, these toner particles are electrostatically deposited on and secured to the charged portions of the image and are not secured on the uncharged or

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background portions of the image. Toner particles deposited on these background portions are physically removed therefrom by the electrostatic action of the carrier particles passing thereacross. The toner particles are electrostatically secured to the rolling carrier particles. The result is an excellent copy of the electrostatic image in the form of an image made up of the toner particles electrostatically clinging to the image-bearing surface and removable therefrom by any of various means such as adhesive transfer or electrostatic transfer. Thus the image may be transferred to a sheet in contact with the image-bearing surface by applying an electrostatic charge to the sheet while in such contact. When the sheet is subsequently stripped from the image-bearing surface it carries with it a substantial proportion of the image to yield a xerographic print which thereafter may be made permanent by any desired method such as heating or solvent fixing.

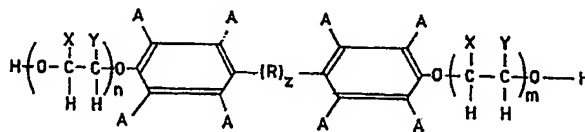
After the image is transferred from the image-bearing surface to the sheet the photoconductive surface may be cleaned and then is ready for use in a subsequent xerographic cycle. The photoconductive surface, after being properly cleaned following a previous xerographic cycle, is in its original condition and is substantially unimpaired for future use. Cleaning the photoconductive surface frequently presents difficulties. A problem of not consistently producing good prints, due apparently to the strong attraction of residual toner particles to the photoconductive surface, has been observed. This problem is evidenced by stubborn adherence of toner particles as such to the surface with the result that after mechanical cleaning operations substantial amounts of toner may still remain on the surface, which builds up on the surface during repeated cycles and eventually requires additional cleaning operations, such as, for example, solvent cleaning.

The cleaning problem is further complicated by the fact that the usual and preferred method of transferring the toner image from the image-bearing surface to the sheet, such as sheet paper, is carried out by affixing the image to the sheet by the application of heat thereby melting the toner and fusing it onto the sheet. Thus, temperatures of melting for the particular toner compositions and, in particular, the resin portion of same must be such that they do not damage the sheet. When paper is the sheet material, such low temperatures are required for melting that a tackiness or stickiness of the toner resin at operating temperatures due to the low melting point of the resin is obtained which further complicates producing good prints. Furthermore, many low melting point resins are very brittle and in xerographic process manipulations tend to degrade to small particle sizes making handling extremely difficult and causing a fine film of toner powder to continually build up on the photoconductive surface. The powder so formed further impairs the clarity of the resultant prints.

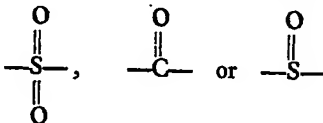
A relatively low melting point, a high degree of abrasion resistance, and the ability to remain untacky at handling temperatures are physical properties which should be present in a toner resin, but proper electrostatic properties are also necessary to achieve a good xerographic toner composition.

Other xerographic processes using the electrostatic compositions of this invention will be set forth below after a discussion of the preparation of the toner compositions of this invention.

According to the present invention there is provided a non-linear polyester resin derived from a dicarboxylic acid and a polyol blend, said polyol blend comprising at least 98 mol per cent of an etherified diphenol characterized by the formula:



wherein Z is 0 or 1; R is an alkylene radical containing from 1 to 5 carbon atoms, a sulphur atom, an oxygen atom, or a radical characterized by the formula:



X and Y are alkyl radicals, containing from 1 to 3 carbon atoms, hydrogen or a phenyl radical, with the limitation that in any X and Y pair on adjacent carbon atoms at least

X or Y is hydrogen; m and n are integers with the proviso that the average sum of m and n in said polyol blend is from 2 to 7; and each A is individually selected from hydrogen and halogen atoms; and from 0.01 to 2.0 mol per cent of an alkoxyated polyhydroxy compound, which polyhydroxy compound contains from 3 to 12 carbon atoms and from 3 to 9 hydroxyl groups and wherein the alkoxyated polyhydroxy compound contains from 1 to 10 mols of oxyalkylene groups per hydroxyl group and said oxyalkylene radical is oxyethylene or oxypropylene; the number of carboxyl groups of said dicarboxylic acid to the number of hydroxyl groups of said polyol blend being in a ratio of from 1.2:1 to 0.8:1.

The present invention further provides an electrostatic composition comprising a toner containing a colouring agent and a polyester resin as defined above, wherein said polyester resin has a liquid point as herein defined of less than 110°C and a tack point as herein defined of more than 60°C.

The colouring agent is either a pigment or a dye or a combination of both. The pigment is usually present at a level of from 1 part to 20 parts and levels as high as 50 parts by weight per 100 parts by weight of the toner have been used. Preferably from 5 to 10 parts by weight of pigment are used.

In one method of preparation of the toner composition of the present invention, the ingredients are thoroughly mixed to form a uniform dispersion of pigment or dye in the resin and the mixed ingredients are finely divided to a desired toner composition particle size. The mixing may be done by various means including combination of the steps of blending, mixing, milling, and presently a preferred method includes the step of blending in a rubber mill to assure uniform dispersion of the pigment in the resin. In an alternate procedure, the polyester resin and the pigment or dye may be mixed together with the polyester resin in a relatively viscous state. The mixture is then cooled and the resulting solid suspension of pigment in polyester resin is ground to the desired particle size. The polyester resin is usually present at a level of from 50 to 99 parts by weight per 100 parts by weight of said toner and preferably from 90 to 95 parts by weight. Usually the toner consists of particles having an average size of less than 40 microns.

As stated above, in addition or instead of the pigment, the toner composition may have a dye present. A dye is normally used where a color reproduction is desired. The dyes are usually present at levels of 2 to 20 parts by weight per hundred parts of toner. Exemplary of the dyes are naphthol B, erichrome B, lithol rubine, phthalocyanine blue, and sulphone thalocyanine blue. Other ingredients of the toner include plasticizers and resin fillers which may improve the handling properties of the toner or adapt the toner for a particular electrostatic printing process. These additional ingredients may be present at levels up to 30 parts per 100 parts of toner by weight.

In the above general formula of the etherified diphenols, an average sum of n and m means that in any polyol blend some of the etherified diphenols within the above formula may have more than 7 repeating ether units but that the average value for the sum of n and m in any polyol blend is from 2 to 7. In a preferred embodiment, the average value for the sum of m and n is from 2 to 4 with a more preferred value being 2 to 3. Examples of compounds within the above general formula are polyoxystyrene-(6)-2, 2-bis(4-hydroxyphenyl) propane; polyoxybutylene-(2)-2, 2-bis(4-hydroxyphenyl)-propane; polyoxyethylene(3)-2, 2-bis(4-hydroxyphenyl) propane; polyoxypropylene(3)-bis(4-hydroxyphenyl) thioether; polyoxyethylene(2)-2,6-dichloro-4-hydroxyphenyl, 2',3',6-trichloro-4'-hydroxyphenyl methane; polyoxypropylene (3)-2-bromo-4-hydroxyphenyl, 4'-hydroxyphenyl ether; polyoxyethylene(2.5)-p,p-bisphenol; polyoxybutylene-(4)-bis(4-hydroxyphenyl)ketone; polyoxystyrene(7)-bis(4-hydroxyphenyl)ether; polyoxypentylene(3)-2,2-bis(2,6-diiodo-4-hydroxyphenyl)propane; and polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane.

A preferred class of etherified bisphenols are those which are ethoxylated or propoxylated and contain 2 to 3 mols of oxyethylene or oxypropylene per mol of bisphenol and have propylene or sulfone radicals as R. Examples of this group include polyoxyethylene (2.5)-bis(2,6-dibromo-4-hydroxyphenyl)sulfone; polyoxypropylene (3)-2,2-bis(2,6-difluoro-4-hydroxyphenyl)propane; and polyoxyethylene (1.5)-polyoxypropylene(1.0)-bis-(4-hydroxyphenyl)sulfone.

Another preferred groups of etherified bisphenols within the class characterized by the above formula are polyoxypropylene 2,2-bis(4-hydroxyphenyl)propane and polyoxyethylene or polyoxypropylene, 2,2-bis(4-hydroxy,2,6-dichlorophenyl) propane wherein the number of oxyalkylene units per mol of bisphenol is from 2.1 to 2.5.

In the polyester resins useful in the electrostatic compositions of this invention, the polyhydroxy composition used to prepare the polyester contains 0.01 to 2 mol per cent preferably 0.1 to 1 mol per cent of an alkoxyated polyhydroxy compound containing

from 3 to 12 carbon atoms and from 3 to 9 hydroxyl groups. A preferred group of polyhydroxy compounds are sugar alcohols, and their anhydrides. Examples of these polyhydroxy compounds are sorbitol; 1,2,5,6-hexanetetrol; glycerol; 1,4-sorbitan; pentaerythritol; xylitol; sucrose; 1,2,4-butanetriol; 1,2,5-pentanetriol; and erythro and threo 1,2,3-butanetriol.

In the alkoxyated polyhydroxy compound, the mols of oxyalkylene groups per mol of polyhydroxy compound is from 1 to 10 times the number of hydroxyl groups of said polyhydroxy compound. The alkylene oxide used in alkoxyating said polyhydroxy compound is ethylene or propylene oxide.

The means of oxide addition in preparing both the etherified diphenols and the alkylene oxide derivatives of the polyhydroxy compounds may be the standard oxide addition techniques well known in the art.

The etherified diphenols used in the preparation of polyester resin compositions of this invention may be prepared by the direct addition of ethylene or propylene oxide to a diphenol or by reacting an olefin halohydrin with a diphenol as disclosed in U.S. Patent No. 2,331,265. Methods of performing the reactions are well known. It should be noted, however, that where mixtures of alcoholic and phenolic hydroxyl groups are present, the alkylene oxides react preferentially with phenolic hydroxyl groups. Thus, when an excess of alkylene oxide is reacted with a diphenol, both phenolic hydroxyls are etherified prior to any extensive ether chains being formed. Therefore, the etherified diphenols illustrated by the above formula will usually have at least one alkylene oxide group attached to each phenolic hydroxyl group residue due to the greater reactivity of the phenolic hydroxyl hydrogen.

The alkoxyated polyhydroxy compounds used in the preparation of the polyester composition of this invention may be prepared by reacting ethylene oxide, propylene oxide, or mixtures thereof with a polyhydroxy compound containing from 3 to 12 carbon atoms and from 3 to 9 hydroxyl groups. A class of such polyhydroxy compounds are mono anhydrides of sugar alcohols, mono saccharides, disaccharides and polyhydroxy alkanes. Among the alkoxyated polyhydroxy compounds included in this class are: polyoxyethylene(10) sorbitol; polyoxyethylene(5) erythritol; polyoxyethylene(4) 1,4-sorbitan; polyoxyethylene(30) pentaerythritol; polyoxypropylene(5) 1,2,3,5,6-hexanepentol; polyoxypropylene(12) sucrose; polyoxyethylene(70) lactitol; and other polyoxyethylene or polyoxypropylene derivatives of hydrogenated polysaccharides, sugars, and anhydrides of polyhydric sugar alcohols. Although the above examples of alkoxyated polyhydroxy compounds utilized only one alkylene oxide in preparing the alkylene oxide derivatives of the polyhydroxy compounds, a mixture of alkylene oxides can also be used. Mixtures of the alkoxyated polyhydroxy compounds may be used in preparing the polyester compositions of this invention. A preferred class of alkoxyated polyhydroxy compounds are those which contain from 1 to 1.5 mols of alkylene oxide per hydroxyl group of the polyhydroxy compound.

The dicarboxylic acids which may be used in preparing the polyester compositions used in accordance with this invention may be either saturated or unsaturated acids. Examples of these acids are maleic acid, fumaric acid, glutaric acid, phthalic acid, isophthalic acid, cyclohexane dicarboxylic acid, terephthalic acid, succinic acid, malonic acid, and the anhydrides of these acids.

In general, the polyester resins of this invention may be prepared by reacting a particular dicarboxylic acid with a polyhydroxy composition disclosed above at a temperature of about 200°C. and under an inert atmosphere. Catalysts or promoters used in preparing polyesters can be added to enhance the activity of the particular reactants.

In general, the novel polyesters of this invention are prepared by the reaction of the polyol blend with the dicarboxylic acid. The reaction may be performed in an inert atmosphere employing moderate temperatures and substantially atmospheric pressure during an early stage to minimize the loss of dicarboxylic acid by volatilization. As the reaction proceeds, the temperature is increased and the pressure reduced. Esterification catalyst may be used although it is generally preferred to carry out the reaction in the absence of excessive amounts of catalyst to avoid contamination of the final polyester product. It is usually desirable to include a small amount of a polymerization inhibitor, such as hydroquinone or pyrogallol, when an unsaturated dicarboxylic acid is used. The reaction temperature used for preparing the final polyesters of this invention will usually include heating to about 200°C. for a portion of the reaction. The resultant polyesters have acid numbers less than about 20. The ratio of the number of carboxyl groups of said dicarboxylic acid to the number of hydroxyl groups of said polyol blend is from 1.2:1 to 0.8:1, it is preferably 1.06:1 to 0.94:1.

The properties which make these resins a unique class are their toughness and their low melting point range. In general, the resins of this invention will have a liquid point

less than 110°C. and a tack point above 60°C. The most desirable resins of this invention have a tack point and a liquid point within 20°C. of one another, and a preferred group of resins have a liquid point which is between 85 and 100°C.

The polyester compositions of this invention are excellent toner resins for use in electrophotographic processes such as xerography and Electrofax. The polyester compositions of this invention which are esters of an ethylenically unsaturated dicarboxylic acid are copolymerizable with ethylenically unsaturated monomers to yield resins useful in the coating, casting, and laminating art. The polyester compositions of this invention are all readily dissolved in ethylenically unsaturated monomers to form a clear, stable solution. The concentration of said ethylenically unsaturated polyester composition in said ethylenically unsaturated monomer may vary from 20 to 80 weight percent of the resulting solution.

Among the numerous copolymerizable ethylenically unsaturated monomers which may be used to dissolve the polyester resins of this invention are styrene, vinyl, toluene, chlorostyrene, divinyl benzene, diallyl phthalate, acrylonitrile, methyl methacrylate, vinyl acetate, ethyl acrylate, α -methyl styrene, vinyl pyridine, and 2-ethyl hexylacrylate.

In preparing mixed resins from an ethylenically unsaturated monomer and the polyester compositions of this invention, conventional reaction initiators, of the kind frequently referred to as "free radical catalysts", may be used to promote the reaction between the polyester composition and the copolymerizable ethylenically unsaturated monomer. Typical of such initiators or catalysts are organic peroxy compounds such as methyl ethyl ketone peroxide, benzoyl peroxide, tertiary butyl perbenzoate, cumene hydroperoxide, and succinic peroxide.

Accelerators for the reaction between the unsaturated polyester composition and the monomer may also be used. Exemplary of such accelerators are dimethyl aniline and cobalt naphthenate.

The polyester resins used in the electrostatic compositions of this invention must have a tack point of greater than 60°C. and a liquid point of less than 110°C. and be physically tough. Preferably the liquid point of the resin is between 85 and 100°C. A better resin is achieved if the liquid point is within the 85 to 100°C. temperature range, and the tack point is at most 20°C. less than the liquid point.

For the purpose of this invention, the liquid and tack points of the resins are determined by using a Kofler Heizbank, Type 7841, hot bench, manufactured by C. Reichert Optische Werke Ag. of Vienna, Austria. This hot bench is an electrically heated variable heat source. First the bench is heated to obtain a 95°C. temperature in the middle of the bench and corresponding lower and higher temperatures at either end of the bench. Then about 5 grams of finely divided resin are sprinkled evenly across the bench surface. The bench temperature at which the resin cannot be brushed from the hot bench using a small artist brush is considered to be the tack point, whereas the bench temperature at which the resin forms liquid globules is considered the liquid point.

As hereinbefore mentioned, the polyester resins which are used in the electrostatic compositions of this invention have to be abrasion resistant, that is they must be tough resins. A procedure for determining the toughness of a resin is to subject particles of a resin to a grinding means and determine how badly the resin has been degraded by the grinding means. A suitable test procedure used to determine the toughness of the resins, used in the toner compositions of this invention, is the following: 115 grams of the polyester resin which has been previously ground to a relatively uniform particle size, that is all the polyester resin particles will pass through a 60 mesh screen but will be retained on a 80 mesh screen, are placed in a size 00 Roalax jar mill by U.S. Stoneware Company with 1,000 grams of Burundum grinding cylinders which are 13/16 inches long \times 13/16 inches in diameter. To prevent caking, 0.5 gram of a silicate anti-caking agent is added. After the mill has been run for approximately 60 minutes, 100 grams of the resin are separated from the grinding cylinders and placed on a series of pre-weighed screens having mesh sizes of 60, 80, 100, 120, 140, and 200 U.S. mesh. A collection pan is placed under the bottommost screen. The screens are placed in descending size order on a Roto-tap shaker and the resin placed on the 60 mesh screen. After 10 minutes of shaking, the resin on each screen and the resin collected on the bottom pan are determined. The polyester resins of this invention are in general sufficiently tough that no more than 35 weight percent of the polyester resin charged to the Roto-tap shaker is collected on the pan and preferably no more than 20 percent is degraded sufficiently to pass the 200 mesh screen. Whenever a resin is said to be abrasion resistant in this application, it will refer to having been tested by the above procedure and having no more than 35 weight percent degraded sufficiently to pass a 200 mesh screen. Furthermore, if a resin is said to have an abrasion resistance of 20,

it will mean that only 20 weight percent of a resin sample tested passed through a 200 U.S. mesh screen.

In order for those skilled in the art to more fully understand the preparation of the resins used in the toner compositions of the instant invention and the preparation of the toner compositions of this invention, the following non-limiting procedures and examples are presented:

EXAMPLE 1

1,865 grams of polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane and 2.9 grams of polyoxypropylene(6) sorbitol are charged to a 3 liter, 4 necked, round-bottom reaction flask which is fitted with a thermometer, a stainless steel stirrer, a glass inlet tube, and a downward condenser. The flask is supported in a GLAS-COL electric heating mantle. Through the glass inlet tube nitrogen gas is allowed to flow sparging the polyol blend and resulting in an inert atmosphere in the reaction vessel. The agitator and heating mantle are then activated and the polyol blend is heated to 50°C. at which time 628 grams of fumaric acid and 1.25 grams of hydroquinone are added to the reaction vessel. The nitrogen gas flow is then regulated at a setting of 2.5 on a SHO-RATE meter of the Brooks Rotometer Company. The reaction mass is heated to a temperature of 210°C. over a period of 5 hours. Water of the esterification reaction is removed as it is formed and the mass is maintained at 210°C. for an additional 6 1/2 hours. The course of the reaction is followed by acid value determinations at hourly intervals. At the end of the reaction, when an acid value of about 20 is achieved, the resin is cooled to room temperature. The resin has an acid value of 13.6, a ball and ring softening point of 104°C., a tack point of 75°C., and a liquid point of 100°C. The ratio of hydroxyl groups and carboxyl groups in the preparation of this resin is 1 to 1.

EXAMPLE 2

According to the procedure of Example 1, 1810.0 grams of polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane and 29.70 grams of polyoxypropylene(6) sorbitol are charged to a reaction vessel. To this polyol mixture is then added 664 grams of fumaric acid resulting in a equivalence ratio of 1 hydroxyl group for every 1.06 carboxyl groups. Also added is 1.25 grams of hydroquinone. As in Example 1, the acid and the hydroquinone are added after the reaction mixture of polyols reaches 50°C. The reaction mixture is then heated to 210°C. and held there until the acid number is less than about 30 at which point the resinous mixture is cooled to room temperature. The resulting polyester has an acid value of 23.8 and a ball and ring softening point of 121°C. It has a tack point of 78°C. and a liquid point of 109°C.

EXAMPLE 3

According to the procedure of Example 1, 1,882 grams of polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane and 1.49 grams of polyoxypropylene(6) sorbitol are added to a reaction vessel. The reaction vessel is heated and sparged with nitrogen. When the reaction mixture reaches 50°C., 616.0 grams of fumaric acid and 1.25 grams of hydroquinone are added. The reaction mixture is allowed to heat to 210°C. at which time the reaction mixture is maintained at 210°C. and the water of reaction is removed. The resin upon completion of the reaction, is cooled to room temperature. This resin has an acid value of 18.1, a ball and ring softening point of 99°C., a tack point of 70°C., and a liquid point of 92°C.

EXAMPLE 4

1,865 grams of polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane is charged to a 3 liter, 4 necked, round-bottom flask fitted with a thermometer, a stirrer, a gas inlet tube, and a condenser for removal of water of esterification. The flask is placed in an electric heating mantle and the heating mantle and the agitator are started. When the temperature in the reaction medium reaches 50°C., 628 grams of fumaric acid and 1.25 grams of hydroquinone are added to the reaction mixture. Nitrogen gas flow is started at a setting of 2.5 on a SHO-RATE meter produced by the Brooks Rotometer Company. The heating is continued with stirring until 210°C. is reached after about five hours. The water of reaction is removed as it is formed through the condenser and the temperature is then maintained at 210°C. The course of the reaction is followed by determining the acid value at hourly intervals. When the acid value reaches a value of about 50, 2.9 grams of polyoxypropylene(6) sorbitol is added to the reaction mixture and the reaction is continued until an acid value of less than about 25 is determined. At this point, the resin is cooled to room temperature and is found to be a solid, friable material.

EXAMPLE 5

In accordance with the procedure of Example 1, 985 grams of polyoxyethylene(3) bis(4-hydroxyphenyl) ketone and 44.3 grams of polyoxyethylene(30) pentaerythritol are placed in a 3 liter, round-bottom flask. This mixture is heated and when the reaction temperature reaches 50°C., 348 grams of succinic acid is added. The reaction mixture is then heated to a temperature of 215°C. and the water of reaction is continually removed. The course of the reaction is followed by taking hourly samples in determining the acid value. After an acid value of 30 is reached the heat is removed and the reaction mixture is slowly cooled to room temperature. The resulting polyester is a hard, tough solid.

EXAMPLE 6

According to the procedure of Example 4, 1520 grams of polyoxyethylene(2) bis(4-hydroxyphenyl) thioether is charged to a 4 liter, round-bottom flask. This dihydric bisphenol is then heated and sparged with nitrogen to maintain an inert atmosphere. When the temperature in the reaction vessel reaches 50°C., 665 grams of phthalic anhydride is added to the reaction vessel. The water of esterification is removed during the heat up period and the continuing reaction period. When 205°C. is reached, 21 grams of polyoxyethylene(15) sucrose is added. The reaction is continued at 205°C. with hourly samples taken and the acid value determined. When the acid value reaches less than 25, the reaction mixture is cooled down. The resulting resin is a hard, friable, tough material.

EXAMPLE 7

According to the procedure of Example 1, 2190 grams of polyoxyethylene(2.5)-2,2-bis(4-hydroxy-2,6-chlorophenyl)propane and 21 grams of polyoxyethylene(12) xylitol are placed in a 4 liter flask. This mixture is heated and when a temperature of 50°C. is obtained; 465 grams of maleic anhydride and 1.25 grams of hydroquinone are added. The heating is continued until a temperature of 210°C. is achieved at which point the temperature is maintained at 210°C. The water of esterification is removed as it is formed through a condenser. The acid value of the reaction mixture is tested at hourly intervals and when the acid number is less than 30, the reaction mixture is cooled to room temperature. The resultant polyester is a tough solid resin.

EXAMPLE 8

According to the procedure of Example 1, 406.8 grams of polyoxypropylene(2)-2,2-bis(4-hydroxyphenyl)propane, 31.2 grams of polyoxypropylene(16)-2,2-bis(4-hydroxyphenyl)propane, 31.8 grams of polyoxypropylene(6) sorbitol, 116 grams of fumaric acid and 0.3 grams of hydroquinone are charged to a reaction vessel. The reaction is allowed to proceed at 210°C. until an acid number of less than 20 is determined. At this point the reaction vessel is removed from the heat source and cooled. The final polyester resin is a hard, tough resin having an acid value of 18.4 and a ball in ring softening point of 108°C.

EXAMPLE 9

The polyester resin of Example 1 is dissolved in 50 weight percent styrene to form a solution having a viscosity of about 500 centipoise. Castings of this solution are cured in a conventional manner, using benzoyl peroxide and heat. The castings are cured for 16 hours at 70°C. and one hour at 90°C. to form a rigid copolymeric composition.

EXAMPLE 10

The polyester resin prepared in Example 3 is blended with 65 weight percent of methylmethacrylate. To this polyester monomer solution is then added a benzoyl peroxide catalyst and mats of fiberglass are coated with the resin solution. The fiberglass mats are stacked and cured in the conventional manner by applying a low heat source. The laminates are thus cured for 16 hours at 70°C. and for one hour at 90°C. to form a relatively inflexible fiberglass laminate.

EXAMPLE 11

The polyester resin of Example 7, is dissolved in 50 weight percent of vinyl toluene to which is added a benzoyl peroxide catalyst. Castings of this solution are cured at 70°C. for 16 hours and then at 90°C. for an additional hour. Flexible copolymeric compositions are obtained which are tough and abrasive resistant.

EXAMPLE 12

According to the procedure of Example 1, 1913.0 grams of polyoxypropylene(4)-2,2-bis(4-hydroxyphenyl)propane and 48.6 grams of polyoxypropylene(6) sorbitol are charged to a reaction vessel. To this polyol mixture is then added 538.4 grams of fumaric acid and 1.25 grams of hydroquinone. The equivalence ratio of hydroxyl groups to carboxyl groups is then equal to one. As in Example 1, the acid and hydroquinone are added after the reaction mixture of polyols reaches 50°C. The reaction mixture is then heated to 210°C. and held there until the acid number is less than about 20 at which time the resinous mixture is cooled to room temperature. The resulting polyester is a solid friable material.

EXAMPLE 13

According to the procedure of Example 1, 2005 grams of polyoxypropylene(6)-2,2-bis(4-hydroxyphenyl)propane, 42 grams of polyoxypropylene(6) sorbitol, 453 grams of fumaric acid, and 1.25 grams of hydroquinone are charged to a reaction vessel. As in Example 1, the acid and hydroquinone are added after the reaction mixture of polyols reaches 50°C. The reaction is allowed to proceed at 210°C. until an acid number of less than 15 is achieved. At this point the reaction mass is cooled to room temperature. The final polyester is a tough resin soluble in unsaturated monomers providing solutions which may be cured to hard thermoset resins.

EXAMPLE 14

614 grams of polyoxystyrene(3) 2,2-bis(4-hydroxyphenyl)sulfoxide, 20 grams of polyoxypropylene(6) erythritol, and 140 grams of succinic acid are charged to a 4 liter reaction vessel. The reaction vessel is then heated to a temperature of 200°C. to 210°C. and maintained within this temperature range for the remainder of the reaction. During the course of the reaction, hourly samples of the reaction mixture are taken and an acid value is determined. When the acid value is less than about 20, the reaction is considered over. The reaction product is removed from the heat source and cooled. The resulting product is a tough, solid polyester resin.

EXAMPLE 15

100 grams of the resin prepared in Example 1 and 10 grams of carbon black pigment obtained from Columbian Carbon Company under the name, "Neo Spectra" Mark II Powder ("Neo Spectra" is a Registered Trade Mark), are blended together in a rubber ball mill to a uniform particle size of about 30 microns. The resulting composition is a xerographic toner useful for black and white prints.

When 1% of this toner is combined with a carrier such as glass beads, in a 2 component developer, similar to those described in U.S. Patent No. 2,618,551, and cascaded across an electrostatic image-bearing surface, the image which is developed by the deposition of the toner on the electrostatic image plate is found to be a clean electrostatic image.

EXAMPLE 16

75 grams of the polyester resin of Example 2 and 5 grams of carbon black are heated to a temperature of 120°C. The resin carbon black mixture is slowly stirred with a magnetic stirrer until the carbon is uniformly dispersed in the liquid resin. The resin carbon mixture is then cooled down to room temperature and ground to a 10 micron size.

In accordance with the procedures of either Example 15 or 16, additional toner compositions are prepared using various pigments at various pigment levels in accordance with the teachings of this invention. The compositions of these toners are presented in Table I. The average particle size of the toners of Examples 17 to 20 is 20 microns.

TABLE I
Toner Compositions

Example	Polyester Resin of Example	Parts by wt. Resin	Pigment	Parts by wt. Pigment	Procedure of Example
17	5	75	Iron Oxide	25	15
18	6	98	Carbon Black	2	15
19	7	94	Carbon Black	3	15
20	8	90	Carbon Black	8	16

EXAMPLE 21

75 grams of the polyester resin of Example 2 and 5 grams of carbon black are heated to a temperature of 120°C. The resin carbon black mixture is slowly stirred with a magnetic stirrer until the carbon is uniformly dispersed in the liquid resin. The resin carbon mixture is then cooled down to room temperature and ground to a 10 micron size.

As stated above, the novel toner compositions of this invention have exceptional utility in developing electrostatic images. In the normal xerographic process, such images are created and developed on the surface of a photoconductive surface which is generally amorphous selenium. However, other photoconductive surfaces, such as those made from a photoconductive pigment such as zinc oxide, zinc cadmium sulfide, tetragonal lead monoxide, or titanium dioxide, incorporated in an insulating resin binder may be used.

In addition, rather than developing the electrostatic image on the photoconductive surface, if desired the electrostatic image may be transferred to an electrically insulating film such as a film of polyethylene terephthalate. This process is described more fully in U.S. Patent No. 2,825,814. The toner composition of the instant invention may then be used to develop the electrostatic image on this insulating film to form a toner image corresponding to the electrostatic image thereon. The resulting toner image may then be either permanently affixed to the insulating film or transferred to a support member as paper, metal or plastics, and the insulating film cleaned and reused in the process.

In any event, as in developing an electrostatic image, the toner composition of the instant invention is electrostatically coated on a suitable carrier surface which is then in turn contacted with the surface bearing the electrostatic image whereby the toner particles are transferred to the surface bearing the electrostatic image to form thereon a powder image corresponding to the electrostatic image. The most widely used method of carrier development is known as cascade carrier development has been referred to above and is more fully described in U.S. Patent No. 2,618,551, U.S. Patent No. 2,618,552, and U.S. Patent No. 2,638,416. In this process the toner is desirably mixed with a granular carrier either electrically conducting or insulating, magnetic or non-magnetic, provided that the particles of granular material when brought in close contact with the powder particles acquire a charge having an opposite polarity to that of the powder particles adhering to and surrounding the granular carrier particles.

The selection of a carrier is an art. If a positive reproduction of the electrostatic image is desired, the carrier is selected so that the toner particles acquire a charge having the opposite polarity to that of the electrostatic image. Alternatively, if a reversal reproduction of the electrostatic image is desired, the carrier is selected so that the toner particles acquire a charge having the same polarity as that of the electrostatic image. Thus, the materials for the granular material are selected in accordance with their triboelectric properties in respect to the toner so that when mixed or brought into contact one material is charged positively if the other is below it in a triboelectric series, and negatively if the other material is above it in a triboelectric series. By selecting materials in accordance with their triboelectric effects, the polarities of their charges when mixed are such that the toner particles adhere to and are coated on the granular carrier particles and also adhere to the electrostatic charges on the photoconductive surface which thus retain the toner in the charge areas that have a greater attraction for the toner than the granular carrier particles have. Typical carrier particles are composed of glass, steel, iron, NH_4Cl , NaCl , and phenolformaldehyde resins.

The carrier particles are at least ten times the size of the toner particles. The carrier particles are shaped to roll across the image-bearing surface. Generally speaking, the carrier particles should be of sufficient size so that their gravitational or momentum force when rolling across the image-bearing surface is greater than the force of attraction of the toner particles for the carrier in the charged areas in order that the granular carrier particles will not be retained by the toner particles. At the same time, the momentum of the carrier must not be so great that it interferes with the toner particles being held or repelled, as the case may be, by the charged or uncharged areas of the plate. It has been found best to use granular carrier particles of a size larger than about 200 mesh, usually between about 20 and about 100 mesh, and toner particles of a size from 1 to 30 microns. The granular carrier particles may, if desired, be somewhat larger or smaller as long as the proper size relationship to the toner is maintained and as long as the granular carrier particles will flow easily over the image surface by gravity when the plate is inclined without requiring additional means or measures to remove them.

The degree of contrast or other photographic qualities in the finished image may be varied by changing the ratio of granular carrier to toner material. Successful results

have been had with from 10 to 200 parts by weight of granular carrier particles capable of being passed through a 20 mesh screen and being collected on a 60 mesh screen to 1 part of the toner having a particle size of 1 to 30 microns. Generally a carrier-to-toner weight ratio in the order of 100 to 1 is satisfactory and preferred compositions run from 70 to 1 to 150 to 1. In such preferred compositions the carrier acts effectively to remove any toner particles which might tend to adhere to a non-image area and the toner itself forms a dense readily transferable and fusible image.

Developer compositions may, therefore, be prepared in accordance with this invention by combining a carrier and a toner within the specific particle size relationship and composition relationship enumerated above. The developers are prepared by simple mixing of the ingredients or by blending in a jar mill, rubber mill, ribbon blender or other mixing device used for solid materials.

Instead of the use of granular particles to provide the carrier surface, the bristles of a fur brush may be used. Here also, the toner particles acquire an electrostatic charge of polarity determined by the relative position of the toner particles and the fur fibers in the triboelectric series. The toner particles form a coating on the bristles of the fur clinging thereto by reasons of the electrostatic attraction between the toner and the fur just as the toner clings to the surface of the granular carrier particles.

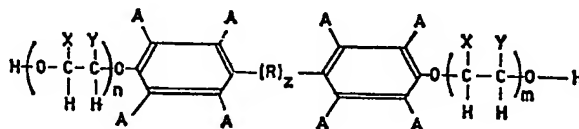
Even more closely related to the cascade carrier development is magnetic brush development. In this process a granular carrier is selected having ferromagnetic properties and selected relative to the toner in a triboelectric series so as to impart the desired electrostatic polarity to the toner and carrier as in cascade carrier development. On inserting a magnet into such a mixture of toner and magnetic granular material the carrier particles align themselves along the lines of force of the magnet to assume a brush-like array. The toner particles are electrostatically coated on the surface of the granular powder carrier particles. Development proceeds as in regular cascade carrier development on moving the magnet over the surface bearing the electrostatic image so that the "bristles" of the magnet brush contact the electrostatic image-bearing surface.

Still another method of carrier development is known as sheet carrier development in which the toner particles are placed on a sheet of paper, plastics or metal. This process is described in U.S. Patent No. 2,895,847. As described therein the electrostatic attraction between the sheet surface and toner particles may be obtained by leading the sheet through a mass of electroscopic toner particles whereby there is obtained a rubbing or sliding contact between the sheet and the toner. Usually it is desirable to spray the surface of the sheet bearing the electroscopic toner particles with ions of the desired polarity as by the use of a corona charging device as described in U.S. Patent No. 2,895,847.

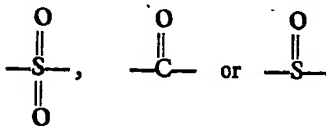
The novel toners of the instant invention may also be formulated to possess both electrostatic and magnetic properties by utilizing a magnetic powdered pigment as the pigment therein. Thus, magnetic iron oxide or similar materials may be used as the pigment in such toners. In this instance substantially larger amounts are used in formulating the toner than when conventional coloring pigments or dyes are used. Thus, a toner having both electroscopic and magnetic properties desirably contains a higher proportion of pigment. In such cases, up to 50% by weight of pigment may be used.

WHAT WE CLAIM IS:—

1. A non-linear polyester resin derived from a dicarboxylic acid and a polyol blend, said polyol blend comprising at least 98 mol per cent of an etherified diphenol characterized by the formula:



wherein Z is 0 or 1; R is an alkylene radical containing from 1 to 5 carbon atoms, a sulphur atom, an oxygen atom, or a radical characterized by the formula:



- X and Y are alkyl radicals, containing from 1 to 3 carbon atoms, hydrogen or a phenyl radical, with the limitation that in any X and Y pair on adjacent carbon atoms at least X or Y is hydrogen; *m* and *n* are integers with the proviso that the average sum of *m* and *n* in said polyol blend is from 2 to 7; and each A is individually selected from hydrogen and halogen atoms; and from 0.01 to 2.0 mol per cent of an alkoxyated polyhydroxy compound, which polyhydroxy compound contains from 3 to 12 carbon atoms and from 3 to 9 hydroxyl groups and wherein the alkoxyated polyhydroxy compound contains from 1 to 10 mols of oxyalkylene groups per hydroxyl group and said oxyalkylene radical is oxyethylene or oxypropylene; the number of carboxyl groups of said dicarboxylic acid to the number of hydroxyl groups of said polyol blend being in a ratio of from 1.2:1 to 0.8:1.
2. A non-linear polyester resin according to claim 1, wherein said alkoxyated polyhydroxy compound comprises from 0.1 to 1.0 mol per cent of said polyol blend.
3. A non-linear polyester resin according to claim 1, or claim 2, wherein the polyhydroxy compound is sorbitol, xylitol, pentaerythritol, glycerol or erythritol.
4. A non-linear polyester resin according to claim 1 or claim 2 wherein said polyhydroxy compound is a monosaccharide, a disaccharide, a monoanhydride of a sugar alcohol, or a polyhydroxy alkane.
5. A non-linear polyester resin according to any one of claims 1 to 4 wherein said ratio of carboxyl groups to hydroxyl groups is from 1.06:1 to 0.94:1.
6. A non-linear polyester composition according to any one of claims 1 to 5 wherein said etherified diphenol is polyoxypropylene2,2-bis(4-hydroxyphenyl)propane; polyoxypropylene2,2-bis(4-hydroxy-2,6-dichlorophenyl)propane; or polyoxyethylene2,2-bis(4-hydroxy-2,6-dichlorophenyl)propane; wherein the mols of ethylene oxide or propylene oxide per mol of bisphenol is from 2.1 to 2.5.
7. A non-linear polyester resin according to any one of claims 1 to 6 wherein the average sum of *m* and *n* in said polyol blend is from 2 to 4.
8. A non-linear polyester resin according to claim 7 wherein the average sum of *m* and *n* in said polyol blend is from 2 to 3.
9. A non-linear polyester resin substantially as described with reference to any one of the Examples.
10. A polyester solution which comprises from 80 to 20 weight per cent of an ethylenically unsaturated monomer and from 20 to 80 weight per cent of an ethylenically unsaturated polyester resin according to any one of claims 1 to 9.
11. A polyester solution according to claim 10 wherein said ethylenically unsaturated monomer is styrene.
12. A copolymer obtained by polymerizing the solution claimed in claims 10 or 11.
13. An electrostatic composition comprising a toner containing a colouring agent and a polyester resin as claimed in any one of claims 1 to 9, wherein said polyester resin has a liquid point as herein defined of less than 110°C and a tack point as herein defined of more than 60°C.
14. An electrostatic composition according to claim 13 wherein said toner comprises particles have an average size of less than 40 microns.
15. An electrostatic composition according to claim 14 wherein the particle size of said toner particles is from 1 to 30 microns.
16. An electrostatic composition according to claim 14 or claim 15 which contains from 70 to 150 parts by weight of carrier particles to each part of toner particles and said carrier particles are at least 10 times as large as said toner particles.
17. An electrostatic composition according to claim 16 wherein said carrier particles comprise glass, iron, steel, NH₄Cl, NaCl or phenol-formaldehyde resins.
18. An electrostatic composition according to any one of claims 13 to 17 wherein said etherified diphenol is an ethoxylated or propoxylated dihydric bisphenol wherein R is propylene or sulphone.
19. An electrostatic composition according to claim 18 wherein the ethoxylated or propoxylated bisphenols contain 2 to 3 mols of oxyethylene or oxypropylene per mol of bisphenol.
20. An electrostatic composition according to claim 19 wherein the polyester resin has a liquid point between 85°C to 100°C and a tack point of at most 20°C less than said liquid point.
21. An electrostatic composition according to any one of claims 13 to 20 wherein the colouring agent is a pigment and is present in an amount of from 1 to 20 weight per cent of the toner composition.
22. An electrostatic composition according to claim 21 wherein said pigment is present in an amount of from 5 to 10 weight per cent of the toner composition.

23. An electrostatic composition according to claim 13 substantially as described with reference to any one of the Examples.

24. A process of xerography wherein an electrostatic image is made visible, comprising contacting a photoconductive surface bearing an electrostatic image therein with an electrostatic composition as claimed in any one of claims 13 to 23.

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